



Short communication

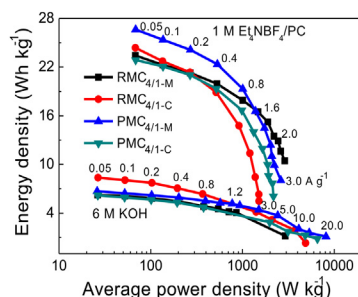
Efficient preparation of biomass-based mesoporous carbons for supercapacitors with both high energy density and high power density

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H I G H L I G H T S

- High performance mesoporous carbons (MCs) for supercapacitors are made from biomass.
- The specific surface area of MC varies from 1527 m² g^{−1} to 1634 m² g^{−1}.
- The energy density of MC supercapacitor reaches 19.3 Wh kg^{−1} at 1007 W kg^{−1}.
- MCs made by microwave heating have higher energy density at higher power density.

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Mesoporous carbons (MCs) with high surface area of 1527–1634 m² g^{−1} for supercapacitors are made from biomass such as peanut shell and rice husk by one-step zinc chloride (ZnCl₂) activation assisted with microwave heating. At higher current density, the MCs made by the microwave heating show both higher energy and higher power density than the MCs made by the conventional heating because of bigger average pore size and unique mesopore structure in the MCs made by the microwave-assisted technique. It has been found that the supercapacitors made from the MCs by the microwave-assisted method have a high energy density of 19.3 Wh kg^{−1} at high power density of 1007 W kg^{−1} in 1 M Et₄NBF₄/PC electrolyte, suggesting that the microwave-assisted one-step ZnCl₂ activation technique is an efficient approach to the production of biomass-derived MCs with high performance for supercapacitors.

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1. Introduction

Supercapacitors are drawing much attention as a promising energy storage device [1]. Porous carbons including mesoporous carbons (MCs) and microporous carbons have been widely used as the electrode materials of supercapacitors due to their high surface area. However, some micropores in traditional porous carbons are not accessible to the electrolyte, limiting the formation of electric

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double-layer to some degree [2]. Because of this, the specific capacitance of microporous carbons drops at higher current density while the MCs show better rate performance [3]. Traditionally, the MCs are mainly produced by the template method [4], which is tedious and not environmentally benign because the template needs to be synthesized before use and be removed by strong acids after the synthesis step. This results in a high production cost of the template MCs. Recently we reported on the synthesis of MCs for supercapacitors from coal tar pitch by coupling KOH activation with MgO template [5]. In comparison to coal tar pitch, the abundant biomass including peanut shell and rice husk is one of the promising carbon precursors for preparing MCs, of which one of the key issues is how to efficiently convert the biomass to the MCs with desired mesopore structures for supercapacitors at low energy consumption and environmental impact. It has been demonstrated that the microwave-assisted heat-treatment has many advantages over the conventional heating process [6,7] in terms of the quick and uniform heating feature, and the low energy consumption [8]. Here we report on a simple method to prepare MCs with well-developed mesopore structure for supercapacitors from peanut shell and rice husk by one-step microwave-assisted ZnCl_2 activation.

2. Experimental

The peanut shell with an ash content of 1.44% on a dry basis (A_d) was obtained from Huai-an in Jiangsu province. The rice husk was obtained from Huai-xiang Company in Anhui province, and before use it was deashed in 0.5 M NaOH solution at 343 K for 2 h under constant stirring to decrease its A_d from 18.44% to 7.00%.

The peanut shell was washed using water and dried, then crushed to a particle size of 3×10 mm, and was impregnated in ZnCl_2 solution for 12 h with a mass ratio of ZnCl_2 /peanut shell of 4/1 while the total mass was kept at 27 g. The ZnCl_2 solution was made by dissolving 21.6 g ZnCl_2 in 60 ml distilled water. The ZnCl_2 -impregnated peanut shell was dried at 383 K for 24 h before being activated to make MCs at a heating rate of 5 K min^{-1} – 1123 K , and held at 1123 K for 1 h in flowing nitrogen by conventional heating [9]. This leads to MCs termed as $\text{PMC}_{4/1-\text{C}}$, where the subscript (C) refers to the conventional heating at a ZnCl_2 /peanut shell mass ratio of 4/1. For comparison, MCs were also made in 20 min by the microwave heating in a LWMC-205-type microwave oven with a microwave power of 600 W [5], which resulted in MCs termed as $\text{PMC}_{4/1-\text{M}}$, where the subscript (M) refers to the microwave heating. The MCs made from rice husk are termed as $\text{RMC}_{4/1-\text{C}}$ and $\text{RMC}_{4/1-\text{M}}$, respectively. Porous carbons made from peanut shell and rice husk without ZnCl_2 activation by conventional heating are termed as $\text{PPC}_{0-\text{C}}$ and $\text{RPC}_{0-\text{C}}$, respectively. In the present study, we have found that porous carbons cannot be made from dried peanut shell or rice husk without ZnCl_2 treatment by microwave heating because of the poor adsorbing capacity of the dried biomass toward the microwave energy [10]. The ash contents for all of the MCs are below 3.2%. The pore structures of the as-made MCs were characterized using nitrogen adsorption–desorption isotherms [5].

Electrodes were made by pressing a mixture of 89 wt% MCs, 5 wt% carbon black with a BET surface area of $550 \text{ m}^2 \text{ g}^{-1}$, and 6 wt% PTFE at 15.0 MPa for 10 s, which were dried at 383 K for 1 h under vacuum before the test [5]. Button-type capacitor was assembled with two carbon electrodes and a separator. For the 6 M KOH electrolyte, the separator used was polypropylene membrane, while for the 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte, the separator was TF4050. The capacitors were evaluated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) by an electrochemical workstation (CHI-760C). The charge–discharge performance of capacitors was tested in a land cell tester (CT-2001A) at

lower current density between 0.05 and 3.0 A g^{-1} [5] and by the supercapacitance test system (SCTS, Arbin Instruments, USA) at high current density of 20 A g^{-1} . The cutoff charge voltage for the supercapacitors using 6 M KOH was set at -0.5 to 0.5 V , while for the 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte, it was set at 0 – 2.7 V .

3. Results and discussion

Fig. 1(a) is the nitrogen adsorption–desorption isotherms of MCs, $\text{PPC}_{0-\text{C}}$ and $\text{RPC}_{0-\text{C}}$, showing clearly that the hysteresis loops are present for all of the MCs, and only a few micropores are formed in $\text{PPC}_{0-\text{C}}$ and $\text{RPC}_{0-\text{C}}$ without adding ZnCl_2 to peanut shell or rice husk. This has evidenced that the well-developed mesopores in MCs made from peanut shell or rice husk can be attributed to the activation of ZnCl_2 . The pore structure parameters of the MCs, $\text{PPC}_{0-\text{C}}$ and $\text{RPC}_{0-\text{C}}$ in different yields are presented in Table 1. Kalderis et al. reported that the ZnCl_2 activation can produce porous carbons with high BET surface area (S_{BET}) of $750 \text{ m}^2 \text{ g}^{-1}$ by the conventional heating [7]. In our case, the S_{BET} of $\text{PMC}_{1/1-\text{M}}$, $\text{PMC}_{2/1-\text{M}}$, $\text{PMC}_{3/1-\text{M}}$, $\text{PMC}_{4/1-\text{M}}$ and $\text{PMC}_{5/1-\text{M}}$ made by microwave-assisted ZnCl_2 activation at different ZnCl_2 /peanut shell mass ratio are 1307, 1454, 1528, 1552 and $1409 \text{ m}^2 \text{ g}^{-1}$, respectively. The $\text{PMC}_{4/1-\text{M}}$ sample with the biggest S_{BET} shows the highest energy density in 6 M KOH aqueous electrolyte. The $\text{PMC}_{4/1-\text{M}}$ performance was further evaluated in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte, which will be discussed below.

Fig. 1(b) is the pore size distribution of MCs, $\text{PPC}_{0-\text{C}}$ and $\text{RPC}_{0-\text{C}}$, in which the macropores are ignorable or poorly developed. The pore size of $\text{PMC}_{4/1-\text{C}}$ and $\text{RMC}_{4/1-\text{C}}$ mainly centers at 1.0 – 2.0 and 2.0 – 10 nm , while for $\text{PMC}_{4/1-\text{M}}$ and $\text{RMC}_{4/1-\text{M}}$, it centers at 1.2 – 2.0

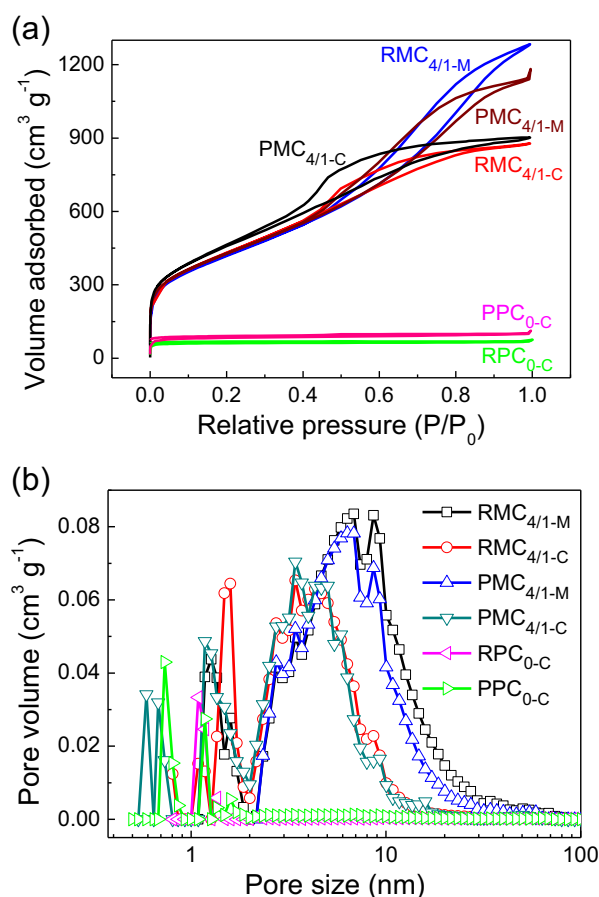


Fig. 1. (a) Nitrogen adsorption–desorption isotherms of MCs, $\text{PPC}_{0-\text{C}}$ and $\text{RPC}_{0-\text{C}}$; (b) pore size distribution of MCs, $\text{PPC}_{0-\text{C}}$ and $\text{RPC}_{0-\text{C}}$.

Table 1The pore structure parameters of MCs, PPC_{0-C} and RPC_{0-C} in different yields.

MC samples	D_{ave} (nm)	S_{BET} (m ² g ⁻¹)	V_t (cm ³ g ⁻¹)	V_{mic} (cm ³ g ⁻¹)	V_{mes}/V_t (%)	Yield (%)
PMC _{4/1-M}	4.52	1552	1.75	0.02	98.9	37.7
PMC _{4/1-C}	3.39	1634	1.39	0.25	82.0	38.9
RMC _{4/1-M}	5.13	1527	1.96	0.02	99.0	32.4
RMC _{4/1-C}	3.46	1565	1.35	0.20	85.2	30.0
PPC _{0-C}	2.11	294	0.15	0.12	20.0	28.7
RPC _{0-C}	1.95	216	0.11	0.09	18.2	27.7

D_{ave} , average pore diameter; S_{BET} , BET specific surface area; V_t , total pore volume; V_{mic} , micropore volume; V_{mes} , mesopore volume.

and 2.0–30 nm, showing that the well-developed mesopores are present. For PPC_{0-C} and RPC_{0-C}, the pore size centers at 0.7–0.8 and 1.0–1.2 nm, which are formed in the pyrolysis step of peanut shell or rice husk. The S_{BET} or yield of PPC_{0-C} and RPC_{0-C} is smaller than that of PMC_{4/1-C} and RMC_{4/1-C}, illustrating that ZnCl₂ has activated the dehydration of peanut shell or rice husk, the degradation of the carbon-containing structures, the charring and aromatization of the carbon skeleton, leading to the creation and formation of more porous structure in MCs. In a word, ZnCl₂ has two functions, i.e. good receptor of microwave energy and chemical activation agent in the microwave-assisted heating. The PMC_{4/1-C} and RMC_{4/1-C} was made at a heating rate of 5 K min⁻¹, while for PMC_{4/1-M} and RMC_{4/1-M}, the average heating rate was 41.1 K min⁻¹ and 36.9 K min⁻¹, respectively. Obviously, due to the high heating rate in the case of

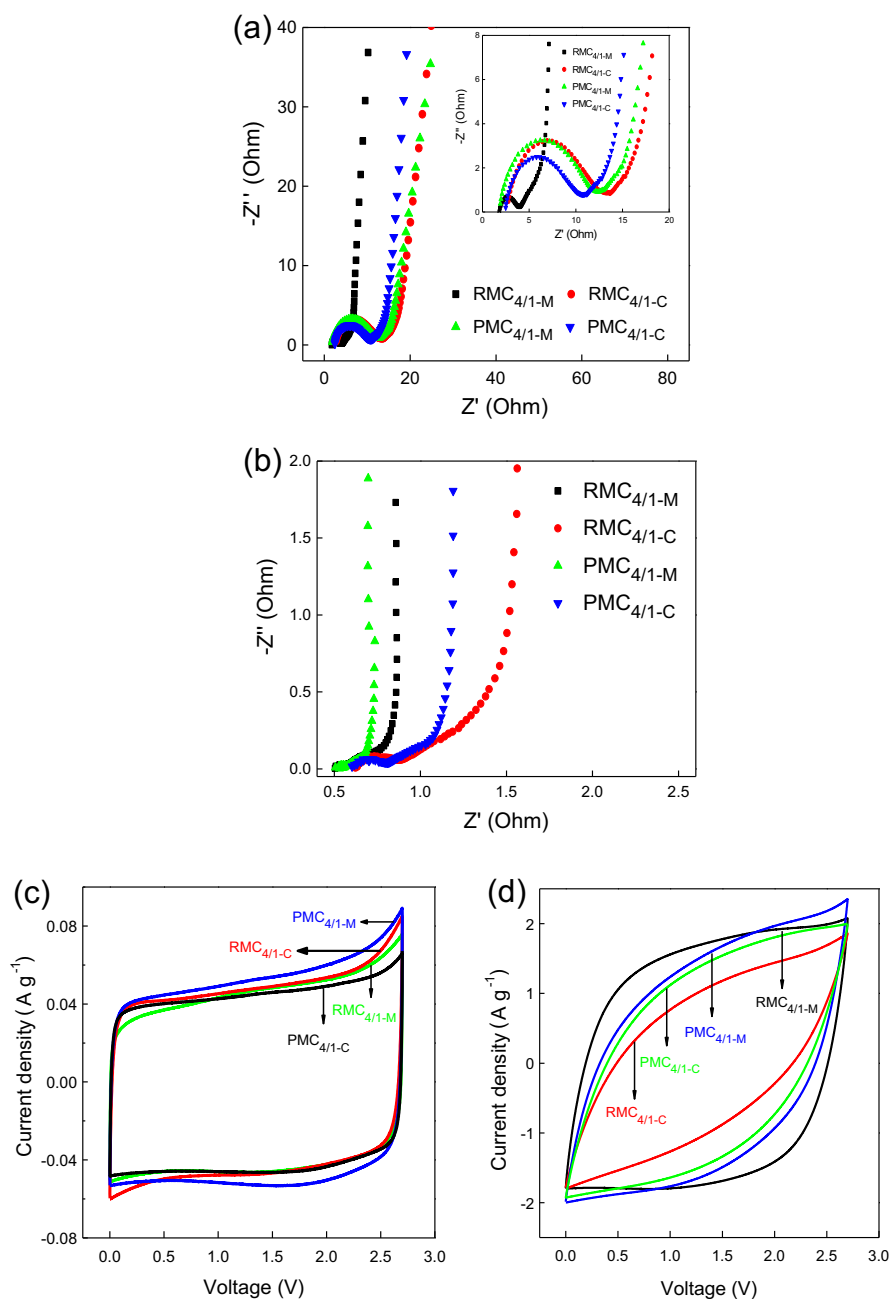


Fig. 2. EIS of MC electrodes in different electrolytes: (a) 1 M Et₄NBF₄/PC; (b) 6 M KOH aqueous solution; CV curves of MC electrodes in 1 M Et₄NBF₄/PC electrolyte at different scan rate: (c) 2 mV s⁻¹; (d) 100 mV s⁻¹.

the microwave heating, the pore size of $\text{PMC}_{4/1-\text{M}}$ and $\text{RMC}_{4/1-\text{M}}$ is bigger than that of $\text{PMC}_{4/1-\text{C}}$ and $\text{RMC}_{4/1-\text{C}}$ in both cases.

Fig. 2(a) and (b) are the EIS of MC electrodes in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte and in 6 M KOH aqueous electrolyte, respectively. All of the MC electrodes have bigger contact resistance in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte than in 6 M KOH aqueous electrolyte. At the high-medium frequency, the MC electrodes show a depressed semicircle. The smaller the diameter of the semicircle, the lower the charge transfer resistance. The smallest charge transfer resistance in $\text{RMC}_{4/1-\text{M}}$ is due to its biggest mesopore size. At the lower frequency range, the curve of $\text{RMC}_{4/1-\text{M}}$ electrode is nearly vertical to the Z^1 axis, showing that the improved capacitance behavior of $\text{RMC}_{4/1-\text{M}}$ is due to its highest mesopore ratio as high as 99.0%.

Fig. 2(c) is the CV curves of MC electrodes at 2 mV s^{-1} scan rate. The symmetric rectangular shapes of the CV curves imply a quick ion diffusion and good charge propagation in all of the MC electrodes at lower scan rate. Fig. 2(d) is the CV curves of MC electrodes at 100 mV s^{-1} scan rate. It can be seen clearly that even at a high scan rate of 100 mV s^{-1} , an excellent symmetric rectangular shape for the CV curves of the MC electrodes can be kept. In comparison with the $\text{RMC}_{4/1-\text{M}}$ and $\text{PMC}_{4/1-\text{M}}$ samples, a large deviation from the rectangular shape is observed in the case of the $\text{RMC}_{4/1-\text{C}}$ and $\text{PMC}_{4/1-\text{C}}$ electrodes due to the limitation in charge transfer processes at higher scan rate that possibly results from the narrow micropores in the MCs made by the conventional way. Compared to the $\text{RMC}_{4/1-\text{C}}$ and $\text{PMC}_{4/1-\text{C}}$ samples, the areas of CV curve of $\text{RMC}_{4/1-\text{M}}$ and $\text{PMC}_{4/1-\text{M}}$ samples are bigger owing to the combining effect of the bigger D_{ave} and V_{mes} percentage as well as their smaller resistance. The specific capacitance of the $\text{RMC}_{4/1-\text{C}}$ and $\text{RMC}_{4/1-\text{M}}$ in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte decreases from 99 F g^{-1} to 79 F g^{-1} and from 94 F g^{-1} to 78 F g^{-1} with the discharge current density from 0.05 A g^{-1} to 3.0 A g^{-1} (a current density increase by a factor of 60), respectively. This is comparable with the carbon that has a specific capacitance in a range of 80 F g^{-1} – 90 F g^{-1} in organic electrolyte [11]. The charge–discharge rate of MCs in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte at higher discharge current density of 5 – 20 A g^{-1} is so quick that a few data during the discharge process can be recorded by the latest SCTS tester. Hence, the specific capacitance of MCs in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte at higher discharge current density of 5 – 20 A g^{-1} is not discussed in detail.

As for the 6 M KOH electrolyte, the variation of specific capacitance of MCs with the current density is shown in Fig. 3(a). It is found that the capacitance of $\text{RMC}_{4/1-\text{C}}$ electrode drops from 245 F g^{-1} to 68 F g^{-1} as the current density increases from 0.05 A g^{-1} to 20 A g^{-1} . The capacitance retention of $\text{RMC}_{4/1-\text{C}}$ electrode is 27.8% while for $\text{RMC}_{4/1-\text{M}}$ and $\text{PMC}_{4/1-\text{M}}$, it is 31.2% and 56.1% because of the synergistic effect of the bigger D_{ave} , V_{mes} percentage and the smaller resistance of MC electrode materials made by microwave heating.

The variation of the energy density of the MC capacitors with the average power density is shown in Fig. 3(b). It is found that the energy density of $\text{PMC}_{4/1-\text{C}}$ capacitor in 6 M KOH electrolyte drops from 6.18 Wh kg^{-1} to 0.83 Wh kg^{-1} with the increase of current density from 0.05 A g^{-1} to 20 A g^{-1} while for the $\text{PMC}_{4/1-\text{M}}$ capacitor, it drops from 6.68 Wh kg^{-1} to 1.10 Wh kg^{-1} . The energy density retention of $\text{PMC}_{4/1-\text{C}}$ capacitor is 13.4% while for the $\text{PMC}_{4/1-\text{M}}$ capacitor, it is 16.5%. For the 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte at higher discharge current density, the energy densities of the supercapacitors made of MCs by microwave-assisted heating are higher than the supercapacitors made of MCs by conventional heating. This is obviously due to the bigger D_{ave} of the MCs made by microwave-assisted heating. The energy density of the $\text{RMC}_{4/1-\text{M}}$ capacitor in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte drops from 23.4 Wh kg^{-1} to 10.4 Wh kg^{-1} with an energy density retention of 44.4%. The energy density of the $\text{PMC}_{4/1-\text{M}}$ capacitor reaches 26.6 Wh kg^{-1} at a current density of 0.05 A g^{-1} . The retention of the energy density of the

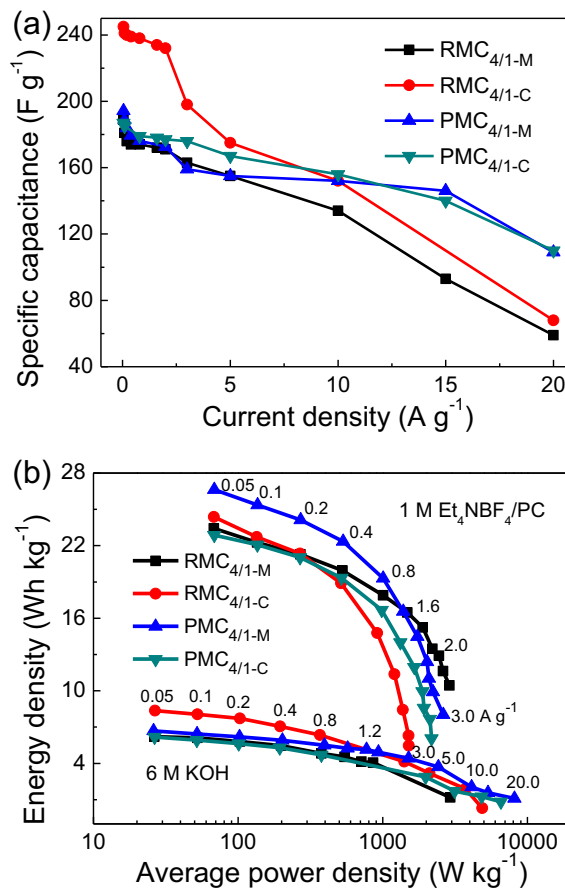


Fig. 3. (a) Specific capacitance of MCs vs. current density in 6 M KOH electrolyte; (b) Energy density of MC capacitors vs. average power density.

$\text{RMC}_{4/1-\text{C}}$, $\text{PMC}_{4/1-\text{C}}$ and $\text{PMC}_{4/1-\text{M}}$ capacitor is 22.5%, 26.6% and 30.5%, respectively. At higher current density, the energy retention for the MCs made by microwave heating is higher than the MCs made by the conventional heating, showing a better rate performance. The average power density of the $\text{RMC}_{4/1-\text{M}}$ capacitor increases from 68 to 2894 W kg^{-1} as the current density increases. The energy density of the $\text{PMC}_{4/1-\text{M}}$ capacitor remains at 19.3 Wh kg^{-1} at a power density of 1007 W kg^{-1} . The energy density of the asymmetric supercapacitor reaches 17.8 Wh kg^{-1} at 400 W kg^{-1} [12], and 15.0 Wh kg^{-1} at 1000 W kg^{-1} [13], respectively. An energy density of 3.5 Wh kg^{-1} at 1958 W kg^{-1} was once reported with hierarchical porous carbons as the electrode materials for supercapacitors [14]. The energy density of the MC capacitors in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte is obviously higher than that of the MC capacitors in 6 M KOH aqueous electrolyte, which increases by 2.5–3.4 times. This is also the case for the average power density. For the MC capacitors in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ organic electrolyte, it increases by 1.6–2.8 times than in 6 M KOH aqueous electrolyte. The results reported here have shown that the MCs with high performance for supercapacitors can be made from peanut shell and rice husk by microwave-assisted one-step ZnCl_2 activation.

4. Conclusions

The MCs for supercapacitors have been made both from the peanut shell and the rice husk by microwave-assisted one-step ZnCl_2 activation. At higher current density in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte, the MCs made by the microwave heating show both higher energy and higher power density than the MCs made by the

conventional heating because of bigger average pore size and unique mesopore structure in the MCs made by the microwave-assisted technique. The energy density of the $\text{PMC}_{4/1-\text{M}}$ capacitor reaches 19.3 Wh kg^{-1} at a power density of 1007 W kg^{-1} . The results have evidenced that the microwave-assisted ZnCl_2 activation technique is an efficient approach to the production of biomass-derived MCs for supercapacitors with high performance.

Acknowledgments

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